

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

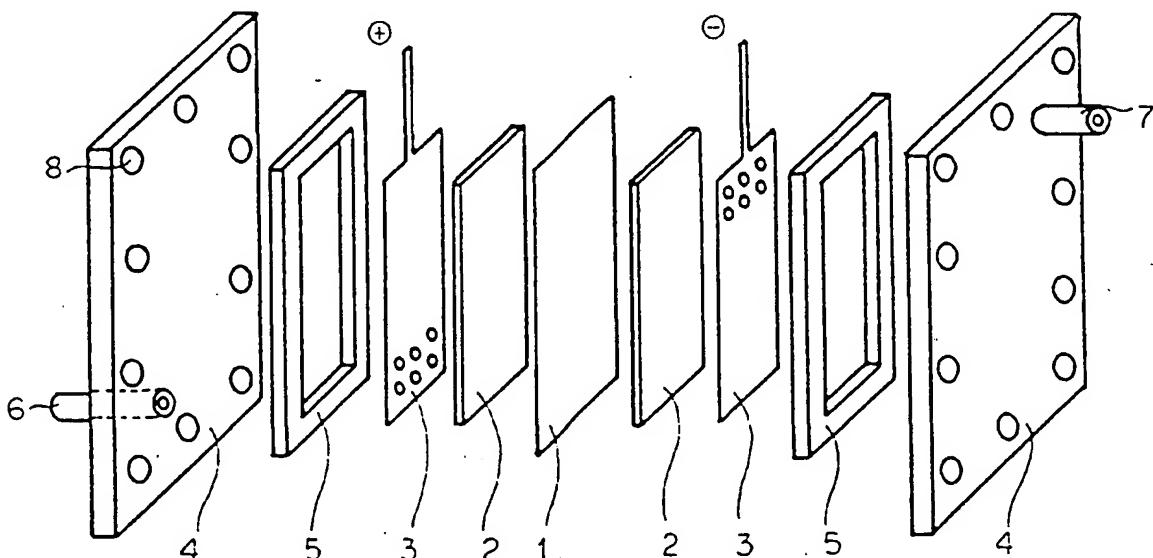


0652-002W01

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 5 : C02F 1/46, B01D 57/02, 61/42, 7/00, 17/06, 15/08, H01G 9/00		A1	(11) International Publication Number: WO 94/26669 (43) International Publication Date: 24 November 1994 (24.11.94)
(21) International Application Number: PCT/US94/05364			(81) Designated States: CA, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).
(22) International Filing Date: 12 May 1994 (12.05.94)			
(30) Priority Data: 5/139354 17 May 1993 (17.05.93)		JP	
(71) Applicant (for all designated States except US): ANDELMAN, Marc, D. [US/US]; 3 Fenimore Road, Worcester, MA 01605 (US).			Published With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.
(72) Inventor; and			
(75) Inventor/Applicant (for US only): OTOWA, Toshiro [JP/JP]; 253, Otowa, Hino-cho, Gamo-gun, Shiga (JP).			
(74) Agent: CROWLEY, Richard, P.; P.O. Box 901, 901 Main Street, Osterville, MA 02655-0901 (US).			

(54) Title: A PLANAR, FLOW-THROUGH, ELECTRIC, DOUBLE-LAYER CAPACITOR AND METHOD OF TREATING FLUIDS WITH THE CAPACITOR



(57) Abstract

The object of the invention is to provide a flow-through, electric, double-layer capacitor providing for a high, steady rate of removal of ionic substances and amenable to commercial scale application and a method of treating fluids using the flow-through electric double-layer capacitor. The invention is a planar, flow-through, electric, double-layer capacitor comprising a separator (1) consisting in an electrically-insulating, porous, flow-through sheet, activated carbon layers (2, 2), each comprising a high specific surface area activated carbon as a main component, collectors (3, 3) disposed externally of the active carbon layers (2, 2), and retaining plates (4, 4) disposed externally of the collectors (3, 3). A fluid containing ionic substances is treated by passing the fluid through the planar, flow-through, electric, double-layer capacitor and repeating, in alternate cycles, application of a direct current constant voltage to collectors (3, 3) and short-circuiting or reversal of connection between collectors (3, 3).

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

DESCRIPTION

**A Planar, Flow-Through, Electric, Double-Layer Capacitor
and Method of Treating Fluids with the Capacitor**Background of the Invention

5 The method is known by which ionic substances are removed from water containing them by the utilization of electrostatic forces using an electric double-layer capacitor.

For example, the specification of U.S. Patent 5,192,432 10 describes a flow-through capacitor for controlled charge chromatography comprising a spirally wound plurality of adjacent layers including a first electrically conductive backing layer, a first high surface area conductive layer, a first non-conductive porous spacer layer, a second 15 conductive backing layer, a second high surface area conductive layer and a second non-conductive porous spacer layer. It is also shown in the same specification that this capacitor finds application in, for example, the purification of water containing ionic substances, such as 20 sodium chloride.

Summary of the Invention

The invention relates to a flow-through, electric, double-layer capacitor of planar configuration utilizing active carbon layers. The invention further relates to a 25 method of treating a fluid containing ionic substances with this flow-through, electric, double-layer capacitor of planar configuration.

The flow-through capacitor disclosed is U.S. Patent 5,192,432 is of interest. However, since this flow-through 30 capacitor comprises a plurality of adjacent layers in a spirally wound form, channeling tends to occur on passage of a fluid, and it was found that when this flow-through capacitor is applied to the purification of a liquid containing ionic solutes, the rate of removal of the ionic 35 substances is not constant but fluctuates and, moreover, the mean rate of removal is fairly lowered. It was thus discovered that this flow-through capacitor can hardly be

employed in the purification of liquids on an industrial scale.

Under the circumstances, this invention has for its object to provide a flow-through, electric, double-layer 5 capacitor providing for high and steady rates of removal of ionic substances and for industrial-scale application and a method of treating fluids with said flow-through, electric, double-layer capacitor.

The planar, flow-through, electric, double-layer 10 capacitor of the invention comprises a separator (1) consisting in an electrically-insulating, porous, flow-through sheet, active carbon layers (2), (2) each comprising a high specific area activated carbon as disposed on either side of said separator (1), collector electrodes (3), (3) 15 disposed externally of said active carbon layers (2), (2) and retaining plates (4), (4) disposed externally of said collector electrodes (3), (3).

The method of treating a fluid according to the invention is characterized in that while a fluid containing 20 ionic substances is passed through said planar, flow-through, electric, double-layer capacitor, application of a direct current constant voltage to the collectors (3), (3) and short circuiting or reversed connection between the two collections (3), (3) are alternately repeated.

25 The invention is now described in detail.

The separator (1) is an electrically-insulating, organic or inorganic sheet across which fluids are ready to flow, such as filter paper, a porous polymer film, a woven cloth or a nonwoven cloth, for instance. The thickness of 30 the separator is about 0.01 mm to 0.5 mm and preferably about 0.02 mm to 0.3 mm.

The active carbon layers (2), (2) are layers each comprising a high specific area activated carbon as a main component. The high specific area activated carbon mentioned above means an activated carbon with a BET 35 specific surface area of not less than 1000 m²/g, preferably not less than 1500 m²/g and, for still better results, 2000 m²/g to 2500 m²/g. When the BET specific surface area of carbon is too small, the rate of removal of ionic

substances from a fluid is low. If the BET specific surface area is too large, the rate of removal of ionic solutes rather tends to decrease, suggesting that it is not mandatory to provide for more than necessary expansion of 5 BET surface area.

The form of activated carbon is optional. Thus, it may, for example, be powdery, granular or fibrous. The powdery or granular activated carbon is used as molded into a board or sheet. The fibrous activated carbon is formed 10 into a web for use. The use of powdery or granular activated carbon in a board or sheet form is costwise by far more advantageous than the use of a web or fabric made of fibrous carbon.

The forming of a board or sheet can be made by, for 15 example, mixing a powdery or granular activated carbon with a binder (polytetrafluoroethylene, phenolic resin, carbon black, etc.) and/or a dispersing medium (solvents, etc.), forming the admixture into a board or sheet and subjecting it to appropriate heat treatment. When such boards or 20 sheets are used as the active carbon layers (2), (2), the boards or sheets may be drilled or otherwise machined beforehand. The technologies relating to the application of an activated carbon board or sheet are disclosed in JP Kokai S-63-107011, H-3-122008, H-3-228814, S-63-110622, S-63- 25 226019 and S-64-1219, among others, and reference can be had to these disclosures.

The thickness of active carbon layers (2), (2) is usually about 0.1 mm to 3 mm, and preferably about 0.5 mm to 2 mm, but this range is not necessarily critical.

30 As the collectors (3), (3), electrodes made of good electrical conductor material, such as copper plates, aluminum plates, carbon boards, graphite foils, etc., and amenable to intimate contact with the active carbon layers (2), (2) are employed. The thickness of collectors (3), (3) 35 is not critical but is about 0.1 mm to 0.5 mm in many instances. For facilitating the application of a voltage, the collectors (3), (3) are usually provided with leads (3a).

The retaining plates (4), (4) are hardly-deformable plates made of electrically insulating material, for example, plastic plates. The retaining guides (4), (4) can be formed with fluid inlet and outlet means, holes for 5 fastening bolts, etc.

Preferably disposed between the collectors (3), (3) and retaining plates (4), (4) are frame-shaped gaskets (5), (5). Instead of providing such independent gaskets (5), (5), the retaining plates (4), (4) may be provided with sealing 10 members.

Using the above component members, a planar, flow-through, electric, double-layer capacitor is fabricated in the construction of retaining plate (4)/gasket (5)/collector (3)/active carbon layer (2)/collector (3)/gasket (5)/15 retaining plate (4).

A fluid containing ionic substances is treated using the planar, flow-through, electric, double-layer capacitor of the above construction. Treatment of a fluid, as the terms are used herein, means not only a treatment for 20 purification of water, conversion of sea water to fresh water, denitrogenation of effluents, etc., but also a treatment for the trapping and recovery of noble metals, purification of inorganic salts, quantitative determination of dissolved ions and so forth. The fluid includes various 25 liquids based upon water or other inorganic solvents, organic solvents or mixtures thereof and even may, for example, be blood. The ionic substance includes electrolytes which are dissociated in solution and chargeable substances, such as metallic salts, amine salts, 30 ammonium salts, inorganic acids, organic acids, etc.

The treatment of a fluid containing ionic substances in accordance with this invention comprises the following steps:

- A planar, flow-through, electric, double-layer capacitor is fabricated and a fluid containing ionic substances is introduced from its fluid inlet by means 35 of a delivery pump, for instance.
- Using a direct current constant voltage source, a voltage of about 0.5 volts to 5 volts (up to about 2

volts in the case of an aqueous solution to avoid electrolysis of water) or in the neighborhood of the above range is applied to the terminals of collectors (3), (3).

5 In the case of an aqueous solution:

• The fluid at the fluid outlet is monitored with a conductivity meter or the like and short-circuiting (or reversal of connection) and voltage application are alternately performed at suitable timings. Time 10 control with a timer is also possible. On short-circuiting (or reversed connection), the ionic substances electrically absorbed on the active carbon layers (2), (2) are desorbed and discharged in concentrated form from the fluid outlet.

15 The principle of treatment of a fluid containing ionic solutes using the planar, flow-through, electric, double-layer capacitor of this invention, taking the case in which said fluid containing ionic solutes is a saline solution, viz. an aqueous solution of sodium chloride, as an example, 20 is illustrated in Fig. 6.

As shown in Fig. 6(a), which represents the voltage application mode, the sodium in the aqueous solution introduced is electrically adsorbed on the active carbon layer (2) adjacent the anode collector (3), while the 25 chloride ion is electrically adsorbed on the active carbon layer (2) adjacent the cathode collector (3), with the result that the sodium chloride concentration of the solution at the outlet is considerably reduced. As the 30 passage of the aqueous solution is continued, the adsorption of the two ions on the active carbon layers (2), (2) reaches a point of saturation so that the sodium chloride concentration at the outlet approaches to the corresponding concentration of the initial solution. As short circuiting or reversal of connection is made between the cathode side 35 and anode side at an appropriate timing, or on the mode represented by Fig. 6(b), the sodium and chloride ions adsorbed on the active carbon layers (2), (2) are desorbed, with the result that an aqueous solution of remarkably increased sodium chloride concentration than the initial

solution is discharged from the fluid outlet. If a contrivance, such as reduction of the rate of passage, is instituted at this time, the sodium chloride concentration of the outlet fluid is further increased.

5 Since the invention utilizes flat, active carbon layers (2), (2) and adopts a clamped, flat assemblage of component parts, the active carbon layers (2), (2) are uniformly compacted so that channeling can be effectively prevented. As a consequence, the rate of removal of ionic substances is
10 stabilized and, in addition, can be enhanced to the practically maximum level.

Examples

The following examples are further illustrative of this invention.

15 Fabrication of a Flow-Through Electric Double-Layer Capacitor

Hardware

Fig. 1 is a disassembled view of the flow-through, electric, double-layer capacitor according to the invention
20 and Fig. 2 is an assembled view of the capacitor of Fig. 1. In Fig. 2, the collectors (3), (3) are shown in sectional view.

25 The following component parts were provided, and the flow-through, electric, double-layer capacitor of Fig. 2 was constructed.

(1) represents a planar separator made of filter paper with a thickness of about 0.2 mm.

30 (2), (2) represent active carbon layers, each measuring 120 mm x 120 mm and having a specific gravity of 0.4. Thus, petroleum coke was activated with potassium hydroxide to provide a granular activated carbon with a high specific surface area (BET) of 2200 m²/g. This carbon was then mixed with polytetrafluoroethylene, carbon black and suitable dispersing medium, and the mixture was compression molded into a 1.0 mm thick board. The proportion of activated carbon in the formulation was 80 weight % and the combined amount of activated carbon in the two active
35 carbon layers (2), (2) was 10 g.

5 (3), (3) represent collectors. Each is made of graphite in the form of a 125 μm thick foil. The lower half of one collector (3) is provided with flow-through orifices (3b) about 1 mm in diameter each, and the upper half of the other collector (3) is provided with similar flow-through orifices (3b). Each of these collectors (3), (3) is further provided with a terminal (3a).

10 15 (4), (4) represent retaining plates. Each is a 10 mm thick polymethyl methacrylate plate. The peripheral margin of each retaining plate (4), (4) is provided with bolt holes (8). Furthermore, one of the retaining plates (4), (4) is provided with a fluid inlet (6) at the lower corner, and the other retaining plate (4) is provided with a fluid outlet (7) at the diagonally opposite upper corner.

20 (5), (5) represent frame-shaped gaskets each 1 mm in thickness. Each is a die-cut piece in the form of a frame from a silicone rubber sheet.

25 The above component members were laid out as illustrated in Fig. 1 and assembled with bolts and nuts (9) to fabricate the flow-through, electric, double-layer capacitor illustrated in Fig. 1.

Treatment of a Fluid-Containing Ionic Substance

Treatment Example 1

30 35 Using the flow-through, electric, double-layer capacitor fabricated as above, with the terminals (3a), (3a) of its collectors (3), (3) being connected to a 1 volt direct current source as shown in Fig. 2, a saline solution of 0.01 mole/ mole concentration was introduced from the fluid inlet (6) of the retaining plate (4) and allowed to flow out from the fluid outlet (7).

The relations between the cumulative volume of saline solution passed and the sodium chloride concentration of the outlet solution at the flow rates of 0.9 ml/min and 9.1 ml/min are plotted in Fig. 3.

It is apparent from Fig. 3 that as a constant voltage of 1 volt was applied, the outlet NaCl concentration fell

rapidly so that a maximum of 93% of sodium chloride was removed at the flow rate of 0.9 ml/min or a maximum of 70% of NaCl was removed at 9.1 ml/min.

Treatment Example 2

5 Fig. 4 is a graph showing the relation between the cumulative volume of saline passed and the sodium chloride concentration of the outlet fluid when saline was passed through the flow-through, electric, double-layer capacitor of Fig. 2, and application of the constant voltage and short 10 circuiting were alternately repeated.

Using the same flow-through, electric, double-layer capacitor fabricated above, with the terminals (3a), (3a) of its collectors (3), (3) being connected to a direct current source of 1 volt, a saline solution of 0.01 mole/æ 15 concentration was introduced at a flow rate of 0.9 ml/min from the fluid inlet (6) of the retaining plate (4) and allowed to flow out from the fluid outlet.

Application of a constant voltage of 1 volt and short-circuiting were alternately repeated according to the timing 20 schedule indicated in Fig. 4, and the concentration of sodium chloride in the solution discharged from the fluid outlet (7) was determined. The results are plotted in Fig. 4.

It is apparent from Fig. 4 that the application of a 25 constant voltage of 1 volt resulted in a sharp decrease in outlet NaCl concentration with 93% removal of sodium chloride, that short circuiting resulted in the discharge of a fluid of about four-fold increased NaCl concentration at the maximum, that as application of the voltage was 30 restarted when the outlet NaCl level had declined close to the concentration of the initial solution, the outlet sodium chloride concentration fell rapidly with 93% removal of NaCl at the maximum, and that the subsequent short circuiting resulted in the discharge of a fluid of about four-fold 35 increased NaCl concentration. It is also clear that since the same results were obtained even when the above pattern was repeated more than 10 times, the stability of this deionizing system is outstanding.

Treatment Example 3

A flow-through, electric, double-layer capacitor similar to the capacitor described under Hardware was fabricated, except that a felt made of fibrous, activated 5 carbon with a BET specific surface area of 1450 m²/g was employed for each of the active carbon layers (2), (2).

Using the above flow-through, electric, double-layer capacitor, with the terminals (3a), (3a) of its collectors (3), (3) being connected to a direct current source of 1 10 volt as illustrated in Fig. 2, a saline solution of 0.01 mole/æ concentration was passed from the fluid inlet (6) of the retaining plate (4) and allowed to flow out from the fluid outlet (7).

The relations between the cumulative volume of the 15 fluid passed and the sodium chloride concentration of the outlet fluid at the flow rates of 1.0 ml/min and 10 ml/min are plotted in Fig. 5. The flow rates are the rates per 10 grams of fibrous carbon constituting the two active carbon layers (2), (2).

20 It is apparent from Fig. 5 that application of a constant voltage of 1 volt results in a sharp reduction of outlet NaCl concentration, and that while the rate of NaCl removal at the flow rate of 1.0 ml/min is very high, the rate of NaCl removal is still high even at 10 ml/min.

Effects of the Invention

As noted in the section of Effect, since the flow-through, electric, double-layer capacitor of this invention employs flat, active carbon layers (2), (2) and comprises a clamped, planar assembly of component members, the active 30 carbon layers (2), (2) are uniformly compacted so that channeling of fluid can be effectively prevented. As a consequence, the stability of the rate of removal of ionic substances is increased and, moreover, the rate of removal can be enhanced to the practically maximum level. 35 Furthermore, since the capacitor is of low profile even when it is scaled up, it is easy to provide for an increased treatment capacity through the arrangement of unit capacitors in a parallel array. Thus, the invention enables the treatment of fluids on a commercial scale.

Brief Description of the Drawings

Fig. 1 is a disassembled view of the flow-through, electric, double-layer capacitor of the invention.

Fig. 2 is an assembled view of the flow-through, 5 electric, double-layer capacitor of Fig. 1.

Fig. 3 is a graph showing the relations between the cumulative volume of saline passed and the outlet NaCl concentration at the flow rates of 0.9 ml/min and 9.1 ml/min in Treatment Example 1.

10 Fig. 4 is a graph showing the relation between the cumulative volume of saline passed and the outlet NaCl concentration when the saline is passed through the flow-through, electric, double-layer capacitor of Fig. 2 and application of a constant voltage and short circuiting were 15 alternately performed in Treatment Example 2.

Fig. 5 is a graph showing the relations between the cumulative volume of saline and the outlet sodium chloride concentration at the flow rates of 1.0 ml/min and 10 ml/min in Treatment Example 3.

20 Fig. 6 is a diagram illustrating the principle of treatment of a fluid containing ionic substances using a planar, flow-through, electric, double-layer capacitor of the invention.

CLAIMS

What is claimed is:

Claim 1. A planar, flow-through, electric, double-layer capacitor comprising a separator (1) consisting electrically-insulating, porous, flow-through sheet, activated carbon layers (2), (2) each comprising a high specific surface area activated carbon as a main component, collectors (3), (3) disposed externally of said carbon layers (2), (2) and retaining plates (4), (4), disposed externally of said collectors (3), (3).

Claim 2. The flow-through, electric, double-layer capacitor of claim 1 including frame-shaped gaskets (5), (5) as interposed between said collectors (3), (3) and retaining plates (4), (4).

Claim 3. A method of treating a fluid characterized in that while a fluid containing ionic substances is passed through the planar, flow-through, electric, double-layer capacitor of claim 1, application of a direct current constant voltage to said collectors (3), (3) and short circuiting or reversed connection between said collectors (3), (3) are alternately performed.

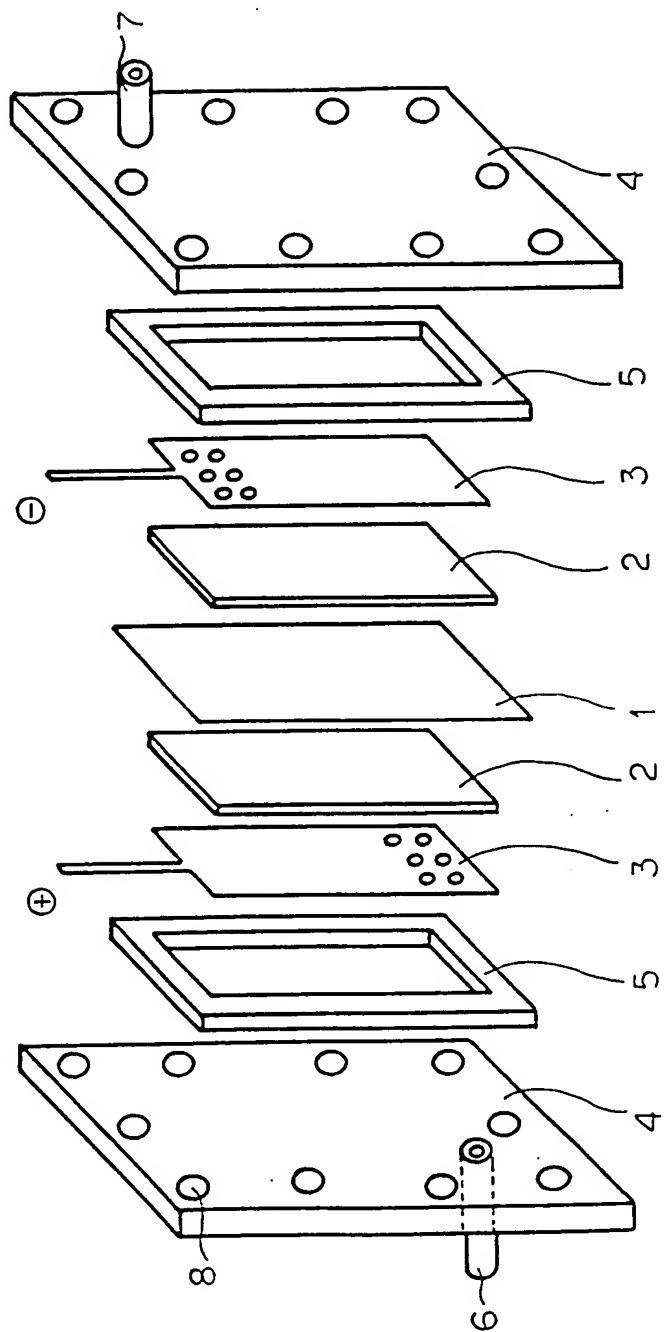


FIG. I

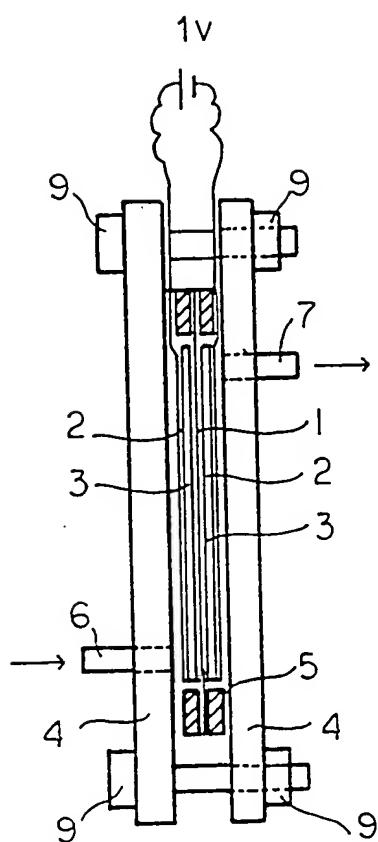


FIG. 2

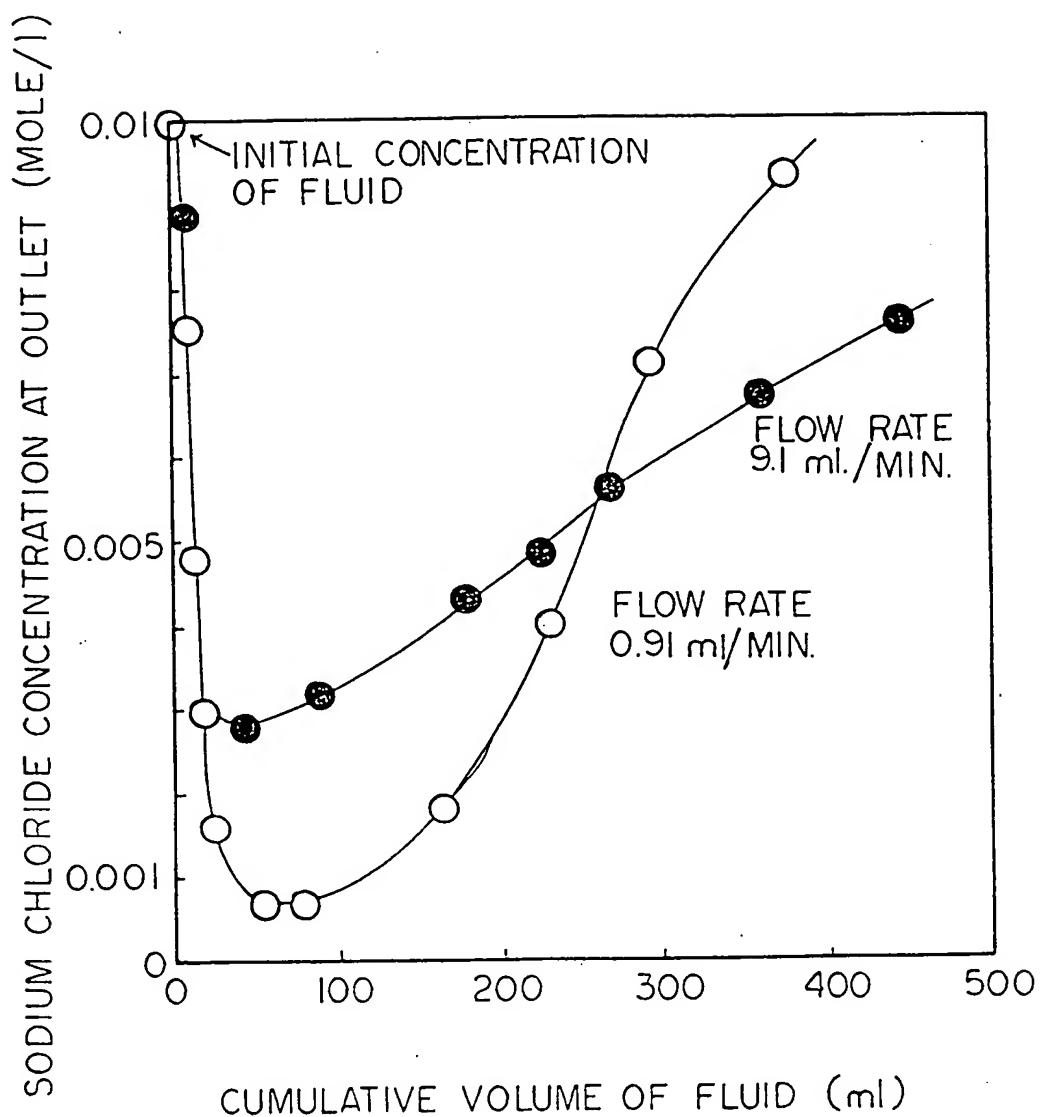


FIG.3

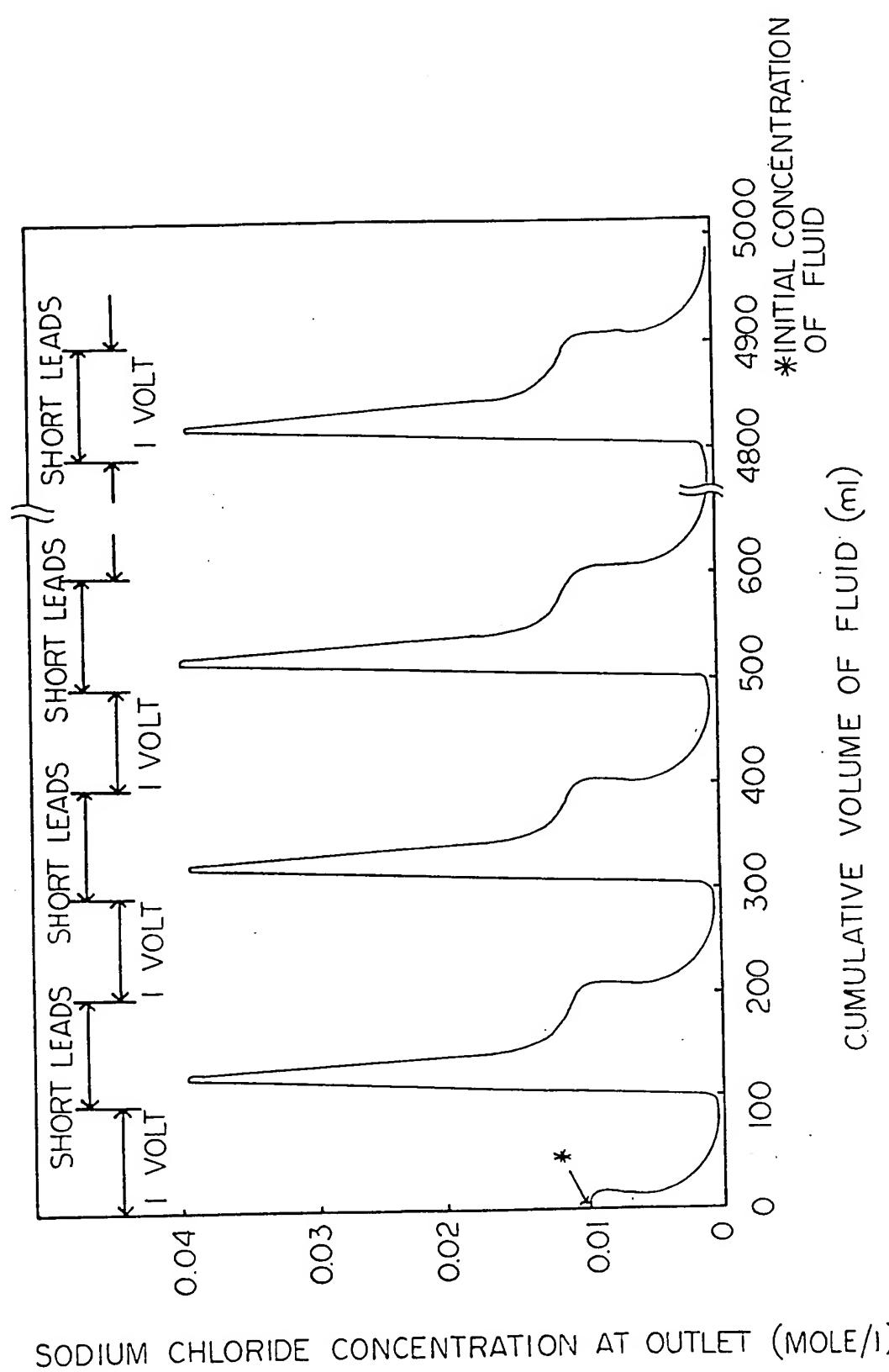


FIG. 4

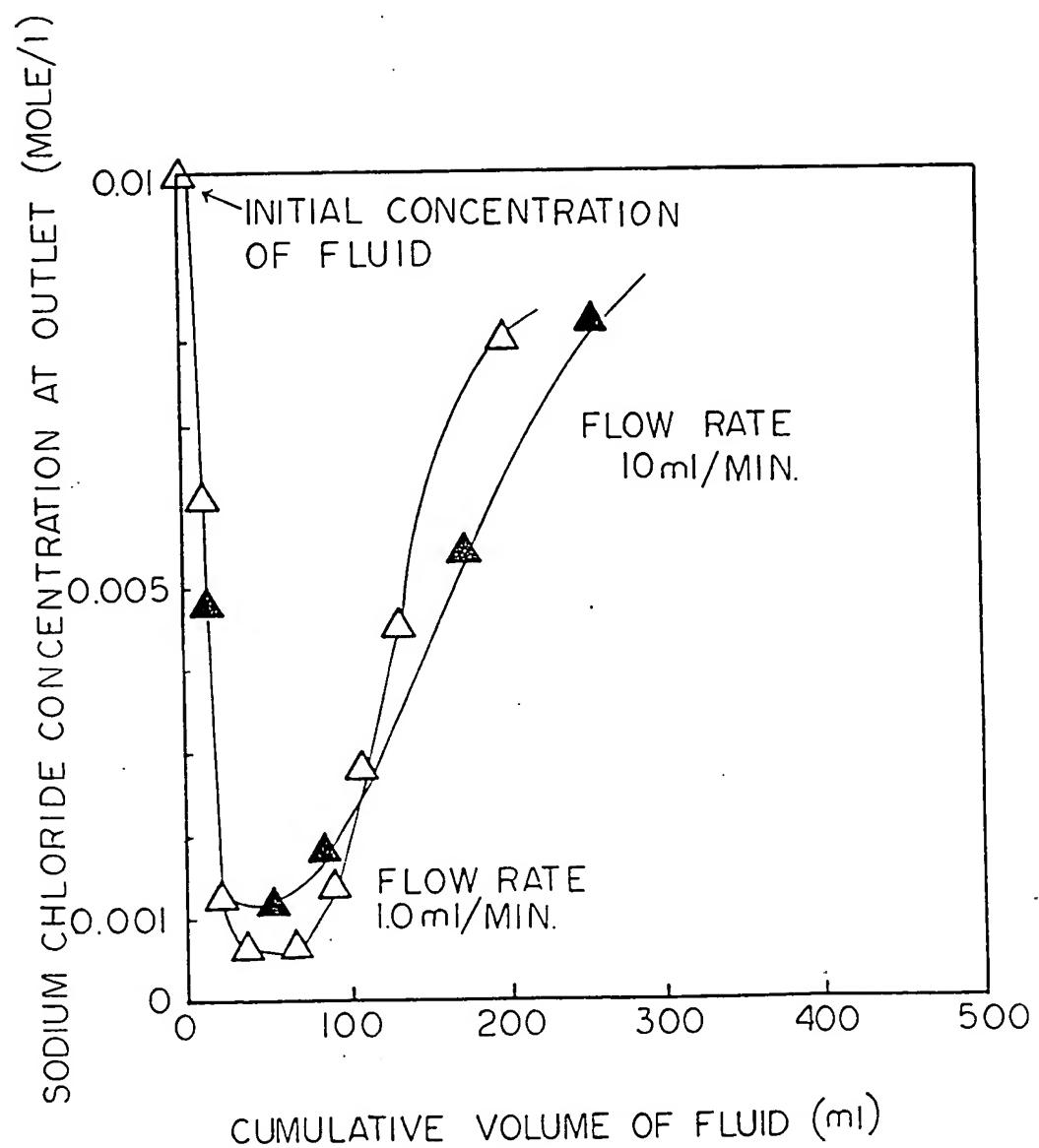


FIG. 5

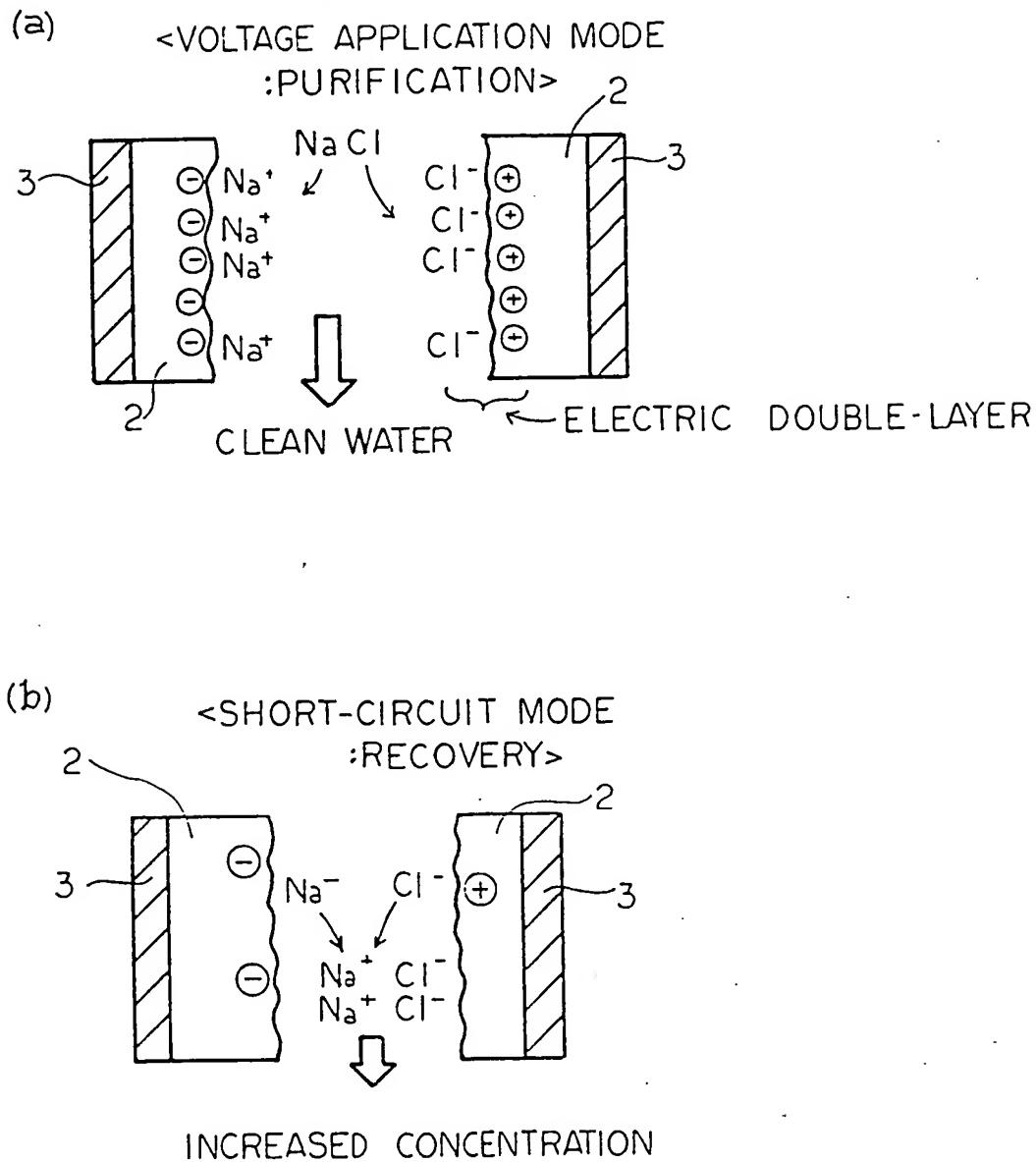


FIG. 6

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US94/05364

A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) :C02F 1/46; B01D 57/02, 61/42, 7/00, 17/06, 15/08; H01G 9/00

US CL : 361/502; 204/180.1, 299r, 149, 302, 305; 210/198.1, 243, 541

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 361/502; 204/180.1, 299r, 149, 302, 305; 210/198.1, 243, 541

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US,A 3,658,674 (Benak) 25 April 1972, figure 1 and col. 4, lines 51-75 and col. 5, lines 1-37	1
---		---
Y		2,3
A	US,A 5,192,432 (Andelman) 09 March 1993, whole document	1-3
A	US,A 5,200,068 (Andelman) 06 April 1993, whole document	1-3

 Further documents are listed in the continuation of Box C. See patent family annex.

• Special categories of cited documents:	• T	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
• A document defining the general state of the art which is not considered to be of particular relevance	• X	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
• E earlier document published on or after the international filing date	• Y	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
• L document which may throw doubt on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	• &	document member of the same patent family
• O document referring to an oral disclosure, use, exhibition or other means		
• P document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search

15 SEPTEMBER 1994

Date of mailing of the international search report

3 SEP 1994

Name and mailing address of the ISA/US
Commissioner of Patents and Trademarks
Box PCTAuthorized officer
MICHAEL SWITZER

C/N